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(54) Microencapsulation of polyisocyanates by interchange of emulsions.

(57) A method of microencapsulation is disclosed whereby two or more organic-in-aqueous emulsions, each containing a reactive component in the organic phase, are mixed together causing the reactive components to react and form polymeric walls around the organic droplets. Either, neither or both emulsions may contain one or more fill materials in their organic phase.

Croydon Printing Company Ltd.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to microcapsules and methods of microencapsulating a core of fill material. The resulting microcapsules are adaptable to a variety of applications, but particularly for use in carbonless copying systems.

Background of the Invention

Microcapsules generally comprise a core of fill material surrounded by a wall or shell of polymeric material. The fill material may be either gaseous, liquid, or solid, and may be composed of a single substance, a solution, a suspension or a mixture of substances. The wall surrounding the core of fill material acts to isolate the fill from the external environment. When it is desirable to release the fill material, the capsule well may be ruptured by mechanical pressure, for example, thereby introducing the fill material into its surroundings. Generally, microcapsules comprise separate and discrete capsules having non-interconnecting hollow spaces for a fill material. The fill material is thus enveloped within the generally continuous polymeric walls of the microcapsules, which may range from 0.1 to approximately 500 microns in diameter.

Uses for microcapsules are as varied as the materials that can be microencapsulated. Of particular importance are the uses of microcapsules in medicinal and biological preparations, fertilizers, flavorings, deoderizers,

adhesives, surface coatings, foams, xerographic toners, and carbonless copying systems.

Though microcapsules and microencapsulation techniques are applicable to a wide variety of products, one of the most significant applications is their use in carbonless copying systems.

The literature contains many methods and techniques for preparing microcapsules, whereby two or more reactive components are brought together to form a microcapsular wall. A majority of these methods from the encapsulating walls by providing minute discrete droplets containing the intended fill material dispersed within a continuous phase that contains at least one of the reactive components. In one class of microencapsulation technique, the walls of the microcapsules are formed from reactive components that are present only in the continuous phase and not within the dispersed droplets. Examples of such microencapsulation methods are the urea-formaldehyde polymerization technique disclosed in U.S. Patent No. 3,016,308 (Macauley) and the coacervation methods described in U.S. Patent No. Re.24,899 (Green). The Macauley patent teaches the formation of a high molecular weight urea-formaldehyde condensate wall from a urea-formaldehyde precondensate that is present in the continuous, aqueous phase. The reaction is carried out by adjusting the pH of the continuous phase. The Green patent discloses forming a gelatinuous coating around oil droplets containing the fill material. This coating is then hardened

into microcapsule walls by cross-linking agents present in the aqueous continuous phase.

A second class of microencapsulation is interfacial polycondensation exemplified by U.S. Patent No. 3,429,827 (Ruus). The method taught by Ruus includes producing an aqueous dispersion of a water immiscible organic liquid containing one of the reactive components. A second reactant is then added to the aqueous phase whereupon the reactants form a polymer wall at the interface between the aqueous and organic phases. For example, the organic dispersed phase may contain compounds such as diacid chloride or mixtures of diacid chloride and disulfonyl chloride, and the aqueous continuous phase may contain compounds such as hexamethylenediamine, ethylenediamine, diethlylenetriamine, triethylenetetramine, tetraethylenepentamine, or mixtures of a polyamine and polyol, such as bisphenol A, thus forming microcapsules having polyamide or copolyamide walls.

One possible disadvantage with the interfacial polycondensation method taught by Ruus is that at least one of the reactive compounds must be soluble in the aqueous phase. Thus, for example, the formation of a micro-

capsule through the reaction of an acid chloride with an aromatic amine, rather than an aliphatic amine, has not been possible via interfacial condensation since aromatic amine compounds are generally insoluble in aqueous solutions. The use of an acid chloride/ aromatic amine pair is not feasible with coacervation techniques because they are not oppositely charged polyelectrolytes. Thus, there is need in the art for a microencapsulation technique that would allow the use of two or more highly reactive components that are both substantially insoluble in aqueous media. Also in U.S. Patent No. 4495509 (European Patent Application No. 84303623.7/0128700 Moore Business Forms Inc) there is described a method of microencapsulation including a) preparing a first organic-in-aqueous emulsion comprising a first solution having a first oil soluble reactive material dissolved therein and a first aqueous emulsification solution, said first oil soluble reactive material being a polyisocyanate and b) preparing a second organic-in-aqueous emulsion comprising a second organic solution having a second oil soluble reactive material dissolved therein and a second aqueous eumulsification solution, said second oil soluble reactive material being an amine.

Another significant use of microcapsules and microencapsulation techniques is the enclosure of highly reactive polyisocyanates. These compounds have a wide variety of applications, including use as a coreactant in forming surface coatings, adhesives, and foams, as is well known in the polymeric arts. Due to the extreme reactivity of most of polyisocyanates, however, it is desirable to isolate them from the external environment until such time as they are reacted with a coreactant to form the desired polymeric product. Various microencapsulation techniques using polyisocyanate compounds have been reported in the literature. For example, U.S. Patents Nos. 4,299,723 (Dahm et al); 4,285,720 (Scher); 4,193,889 (Baatz et al.); (Vassiliades et al.); 3,886,085 (Kiritani et al.); and 3,796,669 (Kiritani et al.) all disclose methods of forming microcapsular walls from the reaction of polyisocyanates with amine compounds. However, all of these patents teach microcapsules formed by interfacial polycondensation techniques. While some limited success may be achieved in microencapsulating polyisocyanates with these and other known methods of microencapsulation, the high reactivity of the polyisocyanate compounds renders them difficult to adequately encapsulate using these older methods. therefore, there is a need in the art for a microencapsulation technique that would allow the easy and effective microencapsulation of polyisocyanates.

It is an object of the present invention to provide an improved method of producing microcapsules.

It is a further object of the present invention to provide methods of producing microcapsules through the interchange of a plurality of emulsions.

It is another object of the invention to provide an improved method of producing microcapsule to encapsulate polyisocyanates.

It is believed that the present invention is directed to a novel class of microencapsulation techniques. Specifically, two organic-in-aqueous emulsions are prepared, each containing at least one oil soluble reactive compound that will react to form polymeric microcapsular walls when brought in contact with each other. The first organic-in-aqueous emulsion comprises a first organic solution having a first oil soluble reactive material (a polyisocyanate) dissolved therein. This first organic solution is then emulsified with a first aqueous emulsification solution to form the first organic-in-aqueous emulsion. The second organic-in-aqueous emulsion includes a second oil soluble reactive material (an amine) dissolved in a second organic solution. The second organic solution is likewise emulsified within a second aqueous emulsification solution such that the second organic-in-aqueous emulsion is formed. The polyisocyanate is present in stoichiometric excess with respect to the amine.

Microencapsulation in accordance with the present invention is obtained by mixing the two organic-in-aqueous emulsions for a time and temperature sufficient to permit the emulsified organic droplets of each emulsion to collide with one another. Collision of two or more emulsion droplets causes the emulsified droplets to exchange at least a portion of their contents. This is believed to occur either through the merger of coalescence of multiple droplets into a single droplet following a collision, or through the exchange of the contents of the droplets during an elastic collision. Regardless of the precise mechanism, however, the contents of colliding droplets are transferred to some extent such that the reactive materials are brought into reactive contact with each other. Thus collisions between droplets of the two emulsions initiate chemical reactions between the reactive materials such that a generally continuous polymeric microcapsular wall is formed around an emulsion droplet, whereby the polyisocyanate is encapsulated.

In the case of an elastic collision, two or more separate microcapsules may be formed, while in the case of a merging collision, only one microcapsule results.

The organic solvents used to dissolve the reactive material with the present invention may be the same for the various emulsions of the present invention or they may be different. Likewise, the aqueous emulsification solutions may be identical for the various organic-in-aqueous emulsions or they may be different. The reactive materials used should be oil soluble and should react to form a polymeric substance suitable for forming a generally continuous microcapsular wall. Many suitable reactive components are well known in the prior art. The present invention is particularly useful where neither of the reactive compounds are sufficiently soluble in aqueous solution to be used with the prior art interfacial condensation or coacervation techniques described above. The present invention may use two or more emulsions, though the use of more than four emulsions would be unnecessary in most instances.

Further objects and embodiments of the present invention will become evident in the following description of the preferred embodiments and claims.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As described in U.S. Patent No. 4495509/European Patent Application No. 843036237/0128700) many compounds can be used in the reactive material to form polymeric capsule walls. Table I below lists some examples of combination of oil soluble reactive compounds contemplated by the invention described in that specification and the type of polymeric wall formed by their reaction.

TABLE 1

Reactive Material 1	Reactive Material 2	Resulting Polymer Wall
Acid Chloride	Amine	Polyamide
Acid Chloride	Bisphenol	Polyester
Sulfonyl Chloride	Amine	Polysulfonamide
Sulfonyl Chloride	Bisphenol	Polysulfonate
Isocyanate	Amine	Polyurea
Isocyanate	Bisphenol	Polyurethane
Bischloroformate	Amine	Polyurethane
Epoxy	Amine	Cured Epoxy

This specification lists many compounds useful in utilizing the invention described. However according to the present invention a polyisocyanate is employed as the first reactive material and an amine is employed as the second reactive material.

Examples of poly-isocyanate compounds that are particularly useful with the present invention are the following: toluene diisocyanate (TDI), 1.4-cyclohexylenediisocyanate, 4.4'-bisphenylene diisocyanate, 4-methly-1.2-phenylene-

diisocyanate, 3.3'-dimethyl-4.4'-biphenylenedisocyanate, 3.3'-dimethoxy-4.4'-biphenylenediisocyanate, 1.4 phenlene-diisocyanate, hexamethylenediisocyanate, octamethylenediisocyanate, p.p'-diphenylmethane diisocyanate, 4-methyl-1,3-phenylene diisocyanate, 2,4,6-trimethyl-1,3-phenylem diisocynanate, bis (3-isocyanaticyclohexyl) methane, 2,4,5,6-tetra-methyl-1,4-phenylene diisocyanate, 1,2-bis (4-isocyanatophenyl) ethane, 2,2-bis (4-isocyanatophenyl) ether, bis (4-isocyanatophenyl) sulfone, 4,4'diphenyl methanediisocyanate, triphenylmethane-pp'p"-triyltriisocyanate, polyisocyanate prepolymers, toluene-diisocyanate alcohol adducts, aromatic/aliphatic polyisocyanate copolymers, modified diphenyl methane diisocyanates polyisocyanurates of toluene diisocyanate, and polymethylene polyphenylisocyanates.

Amine compounds that are useful in connection with the present invention are the following: bis(4-aminophenyl) methane, phenylenediamines including O,p,m -phenylenediamine and 4,5-dimethyl-o-phenylenediamine, naphthalene diamines including 1,5-diaminonaphthalene, 2.2-bis(4-aminophenyl) propane, 2.4-bis(p-aminobenzyl) niline (BABA), bis(p-aminocyclohexyl) methane, bisbexamethylenetriamine (BHMT), bis(4-aminophenyl) ketone, bis(4-aminophenyl) ether, 2,4-toluene diamine, 2,6-toluene-diamine, 3,4-toluenediamine, polymethylene polyphenylamine, 4,4-methylenedianiline, 4,5-diaminoacenaphthene, 3,3-diaminobenzidine, 3,6 diamino durene, 2,7-diaminofluorene, 9,10-diaminophenanthrene and

bis(4-aminophenyl) sulfone. Examples of bisphenol compounds useful in connection with the present invention are as follows: 2.2-bis(4-hydroxyphenyl propane, 2.2-bis(4-hydroxyphenyl) butane, 1.6-dihydroxynaphthalene, 2.7-dihydroxynaphthalene, 4.4'-dihydroxybiphenyl, bis(4-hydroxy-3-methyl phenyl) methane, 1.1 bis(4-hydroxyphenyl) ethane, 3.3-bis(4-hydroxyphenyl) pentane, and bis(4-hydroxphenyl) sulfone.

When a colourless dye precursor is used as the fill material an organic solvent capable of dissolving or suspending the dye precursor must be used. Suitable organic solvents include benzylbutylphthalate (BBP), dibutylphthalate (DBP), toluene, various xylenes, alkylbenzenes, alkylnaphthalenes, and biphenyls. Aqueous emulsification solutions that are useful with respect to the present invention include emulsifiers such as polyvinylpyrrolidone, polyvinyl alcohol, polyethylene glycol, starch, carboxymethylcellulose, and hydroxyethylcellulose, dissolved in water.

In general, a first reactive material, (polyisocyanate) is dissolved within an organic solvent to form the first organic solution. A second reactive material (an amine) is dissolved in a mutual organic solvent, which may or may not be identical to the organic solvent used with the first reactive material. The resulting organic solutions are then separately emulsified into organic-in-aqueous emulsions in the presence of aqueous emulsification solutions. Preferably, the organic droplets formed have sizes in the range of 1 to 20 microns. Different emulsification solutions may be used for the various emulsions or the same solution may be used. The two emulsions are then mixed together and stirred for approximately four to twenty-four hours at room temperature. Alternatively, the two emulsions are mixed together and heated to 30°-80° to complete the reaction between the two reactive materials. During the time that the two emulsions are mixed, droplets from each emulsion collide with droplets of the other emulsion and transfer or merge their contents to some extent. This initiates the reaction between the two reactive materials such that generally continuous polymeric walls are formed surrounding emulsion droplets. The resulting microcapsules are generally within the range 1 to 20 microns and have 5 to 30% of the total microcapsule weight constituting wall material.

In the Patent Specification no. 4495509 proper ratio of the two reactants was determined by using approximately equal equivalent weights even though ratios of equivalent

weights that are greater or less than one may produce better quality or yeild of microcapsules. The present invention however is concerned with the encapsulation of polyisocyanates and it has been found that this may be achieved by using the polyisocyanates in excess as one of the constituents of the micro-encapsulation method and using an amine as its other constituent but using the other techniques as described in that Patent Specification. To encapsulate such a polyisocyanate, the polyisocyanate should desirably be present in stoichiometric excess as compared with the second reactive amine material such that upon completion of the microencapsulation reaction the excess polyisocyanate remains within the interior of the formed microcapsule.

In the following Examples 1-6, microcapsules containing reactive polyisocyanate compounds were formed. These microcapsules are useful as coreactants in forming various foams, adhesives, and surface coatings.

Example 1

Sixty-five parts of Isonate 125M (a, 4,4' - diphenylmethane diisocyanate commercially available from Upjohn Polymer Chemicals) was dissolved in 35 parts of DBP Dibutyl Phthalate. The solution was then emulsified in 125 parts of a 3% Vinol 523 solution (Vinol 523 is a partially hydrolyzed polyvinyl alcohol sold by Air Products and Chemicals, Inc.) using a waring blender until microdroplets of about 1-20 microns were obtained 3.15 parts of BABA 2.4 bis (p-aminibenzyl) aniline was dissolved in 10 parts od DBP and emulsified in 32.5 parts of 3% Vinol 523 solution until particle sizes of about 1-20 microns were obtained. The two emulsions were then mixed in a glass container and stirred with a low speed mechanical stirrer at room temperature for about 24 hours. Under SEM (Scanning electron microscope) spherical microcapsules were observed.

Example 2

72.04 parts of Mondur MRS (a polymethylene polyphenylisocyanate commercially available from Mobay Chemical Corporation) was mixed with 25 parts of DBP and then emulsified in 130 parts of a 3% Vinol 523 solution until particle sizes of between 1-20 microns were obtained.

5.62 parts of BABA in 10 parts of DBP solution was also emulsified similarly in 32.5 parts of 3% Vinol 523 solution. The two emulsions were mixed and stirred for about 20 hours. Under SEM, spherical microcapsules were obtained.

Example 3

56.76 parts of Mondur XP-744 (a modified p,p' - diphenylmethene diisocyanate from Mobay Chemical Corporation) was emulsified in 97.5 parts of a 3% Vinol 523 solution until microdroplet particles of about 1-20 microns were obtained. 3.81 parts of BABA in 10 parts of DBP solution were similarly emulsified in 32.5 parts of 3% Vinol 523 solution. The two emulsions were then stirred together at room temperature for about 16 hours, after which microcapsule formation was observed under SEM.

Example 4

56.2 parts of Isonate 143L (a modified diphenylmethane diisocyanate from Upjohn Polymer Chemicals) was emulsified in 97.5 parts of a Vinol 523 solution until microdroplet sizes of about 1-20 microns were obtained. 4.37 parts of BABA in 10 parts of DBP solution was also similarly emulsified in 32.5 parts of 3% Vinol 523 solution. The two emulsions were then mixed and stirred at room temperature for about 16 hours. Microcapsules were obtained as observed under SEM.

Example 5

58.07 parts of Mondur CB-75 (a toluene diisocyanate-alcohol adduct obtained from Mobay Chemical Corporation) was emulsified in 97.5 parts of 3% Vinol 523 solution until

particle sizes of 1-30 microns were obtained. 2.5 parts of BABA dissolved in 10 parts of DBP solution was also emulsified in 32.5 parts of 3% Vinol 523 solution. The two emulsions were then mixed and stirred together at room temperature for about 16 hours, at which time microcapsules were observed under SEM.

Example 6

58.28 parts of Mondur HC (an aromatic/aliphatic polyisocyanate copolymer from Mobay Chemical Corporation) was emulsified in 97.5 parts of 3% Vinol 523 solution until particle sizes of about 1-30 microns were obtained. 2.29 parts of BABA in 10 parts of DBP solution was also emulsified in 32.5 parts of 3% Vinol 523 solution. The two emulsions were then mixed and stirred together at room temperature for about 16 hours. Microcapsules were obtained as evidenced by SEM observation.

It is to be understood that the above specification emphasizes certain embodiments and features of the present invention and that many embodiments not specifically described above may come within the spirit and scope of the present invention as claimed hereafter.

CLAIMS

1. A method of making microcapsules having generally continuous polymeric walls comprising the following steps:

a) preparing a first organic-in-aqueous emulsion comprising a first organic solution having a first oil soluble reactive material dissolved therein and a first aqueous emulsification solution.

b) preparing a second organic-in-aqueous emulsion comprising a second organic solution having a second oil soluble reactive material dissolved therein and a second aqueous emulsification solution, and

c) mixing said organic-in-aqueous emulsions such that said oil soluble reactive materials react to form said microcapsules characterized in that the first oil soluble reactive material is a polyisocyanate and the second oil soluble reactive material is an amine and so arranged that the microcapsules encapsulate the first oil soluble reactive material.

2. The method of Claim 1 characterized in that the polyisocyanate is present in stoichiometric excess with respect to said amine.

3. Microcapsules having generally continuous polymeric walls prepared by a method comprising the following steps:

a) preparing a first organic-in-aqueous emulsion comprising a first organic solution having a first oil soluble reactive material dissolved therein and a first aqueous emulsification solution,

b) preparing a second organic-in-aqueous emulsion comprising a second organic solution having a second oil soluble reactive material dissolved therein and a second aqueous emulsification solution, and

c) mixing said organic-in-aqueous emulsions such that said oil soluble reactive materials react to form said microcapsules characterized in that the first oil soluble reactive material is a polyisocyanate and the second oil soluble reactive material is an amine and so arranged that the said microcapsules encapsulate the first oil soluble reactive material.

4. The microcapsules of Claim 3 wherein said polyisocyanate is present in stoichiometric excess with respect to said amine.